NEW SYNTHETIC METHOD AND CHARACTERIZATION OF CERAMIC FILMS PREPARED BY ANODIC OXIDATION OF ALUMINUM UNDER SPARKING DISCHARGE

M. Yamada, I. Mita

JOURNAL DE PHYSIQUE
Colloque C1, supplément au n°2, Tome 47, février 1986 page C1-181

NEW SYNTHETIC METHOD AND CHARACTERIZATION OF CERAMIC FILMS PREPARED BY ANODIC OXIDATION OF ALUMINUM UNDER SPARKING DISCHARGE

M. YAMADA and I. MITA*

College of Science and Technology, Nihon University, 1-8, Kanda Surugadai, Chiyoda-ku, Tokyo, 101, Japan
**The Tokyo Metropolitan Industrial Technology Centre, 13-10, Nishigaoka 3-chome, Kita-ku, Tokyo, 115, Japan*

Résumé - Une nouvelle méthode de synthèse de films céramiques, par oxydation anodique de l'aluminium, a été réalisée. Leurs cristaux sont pour la plupart des η-alumines et contiennent peu de α-alumines. Ces films peuvent incorporer toutes sortes de métaux grâce aux procédés électrochimiques

Abstract - A new synthetic method of ceramic films by anodic oxidation of aluminum was developed. Most of the crystals in the films are composed of eta or alpha-alumina. These ceramic films can incorporate a lot of metals by electrolytic methods.

I - INTRODUCTION

This paper concerns about synthesis of cristalline alumina films on aluminum by the method of anodic oxidation of aluminum for the purpose of preparing new type of ceramic films. It have been found that gamma and alpha alumina films on aluminum prepared anodization by Tajima, S. et al.1) and Lautenchlager, W. et al.2). Present authors found a two-step anodic oxidation method to obtain eta and alpha alumina films, with metal incorporated, by means of the anodic oxidation of aluminum with sparking discharge under high voltage. These crystalline alumina films on aluminum are new type ceramic films and expected to have excellent physical properties compared with usual amorphous alumina films by anodization.

II - EXPERIMENTAL METHODS

Aluminum plate (0.5 mm thick) of 99.99% and 99.85% purity and aluminum foil (0.1 mm thick) of 99.99% purity were used. These specimens were degreased by the usual method using aq. solutions of sodium hydroxide and then rinsed with distilled water.
Conditions of anodization:
(A) Amorphous alumina film on aluminum was prepared by anodic oxidation of aluminum in 15% sulfuric acid at 25°C with current density of 1.0-2.0 A/dm^2d.c. for 17-34 min.
(B) Crystalline alumina film (type eta) on aluminum was prepared by anodic oxidation with sparking discharge, that is, the film was prepared in 2M aq. solution of sodium carbonate with 10-20 A/dm^2 d.c. at 30-80°C for 3-5 min.
(C) Crystalline alumina film (type alpha) on aluminum was prepared by anodic oxidation with sparking discharge in molten sodium bisulfate-ammonium bisulfate mixture (mol ratio: 1:1.15) with current density of 10 A/dm^2 d.c. for 10 min.
Electrolytic coloring process:

Aluminum plate was anodized in the electrolyte, with metal salts added, under the conditions (B) of (C).
Coloring by dipping process:
Amorphous alumina film on aluminum was dipped in aq. solution of metal salts. The film was reanodized under the conditions (A) or (B).

III - RESULTS AND DISCUSSION

III-1 Observation of the film surfaces
Electron micrographs of four kinds of alumina films are shown in Photo. 1.
Photo. 1-a shows the transmission electron micrograph of amorphous alumina film prepared by anodic oxidation of aluminum under the condition (A). Photo. 1-b shows the scanning electron micrograph of the crystalline alumina film (type eta) by anodic oxidation of aluminum under the condition (B). Photo. 1-c shows the film prepared by reanodization of amorphous alumina film under the condition (B). Photo.1-d shows scanning electron micrograph of the crystalline alumina film (type alpha) prepared by reanodization of amorphous alumina film under the condition (C).
The amorphous alumina film has many pores of almost same size, while shape of the pores of the crystalline alumina film are not uniform. Appearance of the crystalline alumina film (type eta and alpha) is different from that of the amorphous alumina film. From these photographs, it is seen that the effects of different anodizing conditions appeared clearly on the film surfaces. 6)

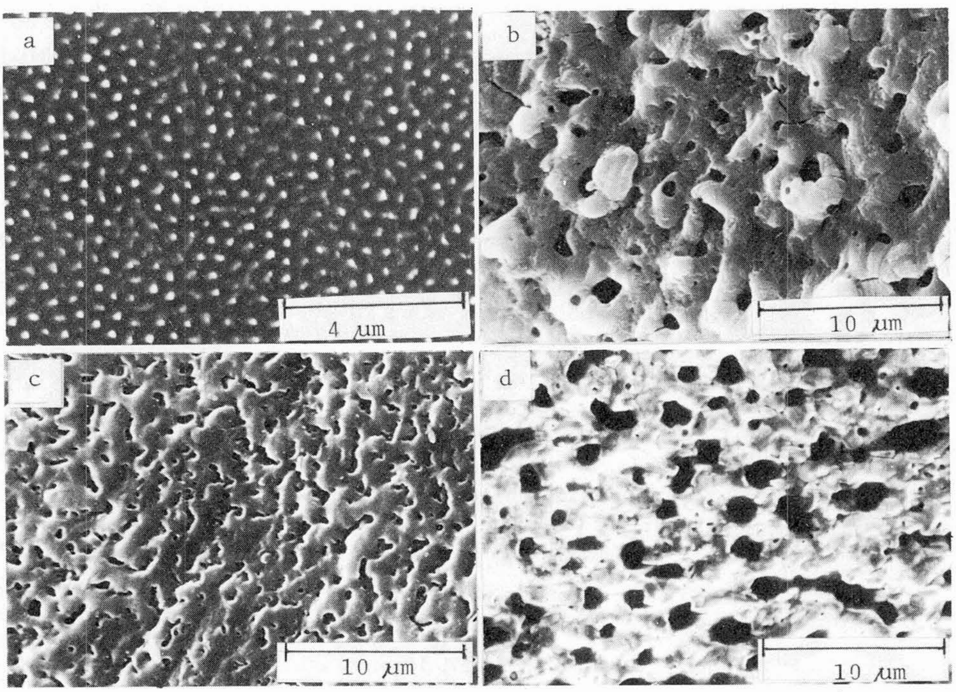

Photo. 1. Electron micrographs of alumina films prepared by anodic oxidation of aluminum.

a: TEM of amorphous alumina film prepared by condition (A).
b: SEM of eta alumina film prepared by condition (B).
c: SEM of eta alumina film prepared by reanodization of amorphous alumina film, condition (A)⟶(B).
d. SEM of alpha alumina film prepared by reanodization of amorphous alumina film, condition (A)⟶(C).

III -2 Crystal structure of the alumina films

Four kinds of the alumina films were peeled off from aluminum substrate, washed, dried and powdered. Fig.1 shows X-ray diffraction patterns of four kinds of alumina. Fig. 1-a and 1-b respectively show amorphous alumina prepared in sulfuric acid under the condition (A) and crystalline alumina (type eta) prepared in sodium carbonate solution under the condition (B). Fig. 1-c shows crystalline alumina prepared by reanodization of amorphous alumina film under the condition (B). This alumina was mainly composed of mixure eta alumina with traces of alpha alumina. Fig. 1-d shows crystalline alumina prepared in bisulfate by reanodization of amorphous alumina film under the condition (C). This alumina is mainly composed of alpha alumina with traces of eta alumina. These crystalline aluminas seen to be formed by local heating caused by the breakdown anodic oxidation accompanying the sparking discharge on the anodic surfaces, under high electric voltage. 3)4)5).

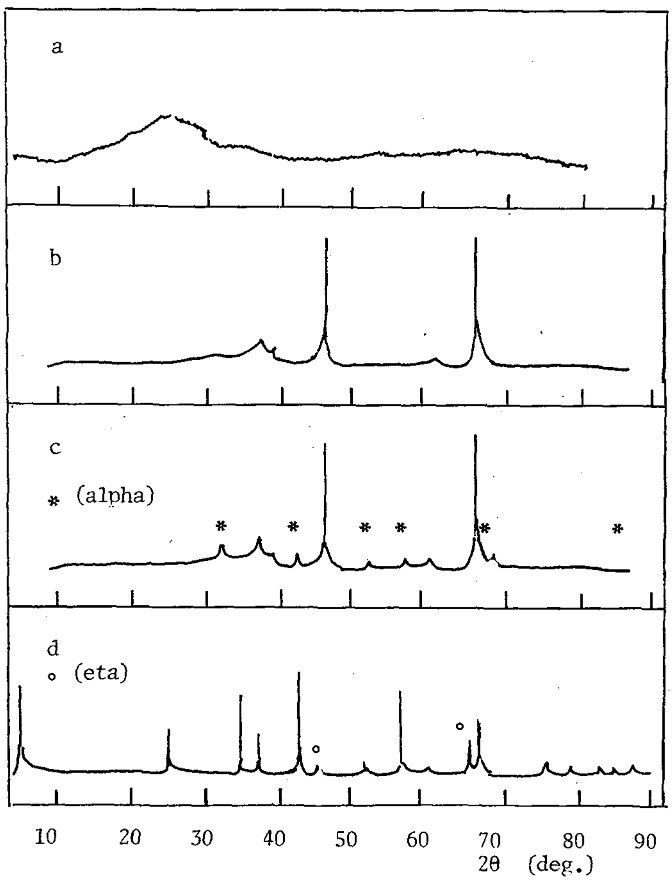

Fig. 1. X-ray diffraction patterns of alumina films prepared by anodic oxidation of aluminum.

a: amorphous alumina prepared by condition (A).
b: eta alumina prepared by condition (B).
c: eta alumina prepared by reanodization of amorphous alumina film, condition (A)⟶(B).
d: alpha alumina prepared by reanodization of amorphous alumina film, condition (A)⟶(C).

III-3 Colored eta alumina by electrolytic coloring process

For incorporating chromium or ferric ions into the eta alumina films, the following electrolytic coloring process, under high voltage with sparking discharge, was carried out. Aluminum was anodized in 2M sodium carbonate, added with aq. solution of ammonium chromate or ferric ammonium oxalate. Eta alumina film prepared in an electrolyte containing chromate or ferric ion was colored sepia or gray respectively. Color of the film prepared in the electrolyte containing only sodium carbonate is silver or white, while the color depends on the added metal salts in the electrolyte. Table 1 shows the favorable conditions. These results show that colored eta alumina film can be prepared by electrolytic coloring process under high voltage with sparking descharge. [6]

Table 1. Anodizing conditions and color of the film prepared by electrocoloring. [6]

color & conditions \ electrolyte	Na_2CO_3 (2 M)	
	$(NH_4)_2CrO_4$	$(NH_4)_2Fe(C_2O_4)_3$
Temp. (°C)	60	40
Time (min)	4.5	3.5
Current density (A/dm^2) d.c.	8	10
Color	Sepia	Gray

III-4 Colored eta alumina by dipping and reanodizing process

Yellow amorphous alumina film was prepared by dipping an amorphous alumina film in aq. solution of ammonium chromate. The film was reanodized in 2M sodium carbonate under the condition (B). Color of the film changed from yellow to deep redish-violet. The film shows clear red fluorescence under irradiation of UV light in a dark room since the optical properties of this film are similar to the "RUBY FILM" previouly reported. 3) That is, this film seems to be transformed partially into alpha alumina from amorphous alumina via eta alumina.

III-5 Alpha alumina films incorporated with various metal ions

Table 2 shows color and fluorescence of alpha alumina films, with metal ions incorporated, obtained by two-step anodic oxidation process. Metal ions were absorbed into the pores of the amorphous alumina films by single or alternative dipping method. As shown in the table, alpha alumina films with chromium ions incorporated have reddish violet color and red fluorescence, while those with Fe, Pb, Ni, Cd, and Co show violet or dark violet fluorescence.

Table 2 Color and fluorescence of the alumina films obtained by two-step anodic oxidation 5)

Absorbed inorganic compounds	Alumina films	
	Color	Fluorescence
Single dipping process		
$(NH_4)_2CrO_4$	light reddish violet	deep red
$Fe_2(C_2O_4)_3Na_2C_3O_4$	yellowish light gray	dark violet
Alternate dipping process		
$Pb(COOH)_2 + K_2Cr_2O_7$	light reddish violet	red
$K_2Cr_2O_7 + AgNO_3$	light reddish violet	red
$Ni(COOH)_2 + (NH_4)_2S$	yellowish light gray	dark violet
$CdSO_4 + (NH_4)_2S$	light gray	bright violet
$Co(COOH)_4 + Na_2S$	light gray	bright violet

III-6 RUBY FILM

Alpha alumina film, with chromium ion incorporated, was peeled off form the aluminum substrate, and optical properties of the film studied.
Since the film shows absorption peaks at 410 and 560 nm similar to the peaks of a synthetic ruby prepared by Verneuil method (Fig. 2), hereafter we call this film as "RUBU FILM". 5)

The fluorescence of the ruby film and the synthetic ruby have the same peak wavelength (Fig. 3) under the excitation of light of 410 nm. Coloration of the ruby film seems to be caused by trivalent chromium ions replacing trivalent aluminum ions in the alpha alumina structure.

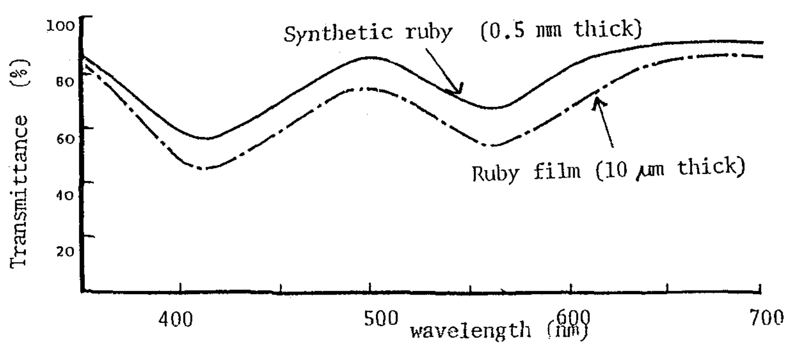

Fig. 2. Absorption spectra of ruby film prepared by anodic oxidation of aluminum and synthetic ruby prepared by the Verneuil method.

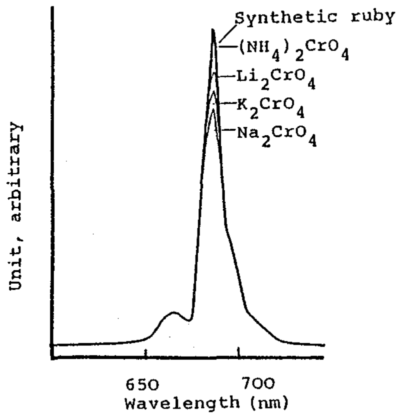

Fig. 3. Effect of chromate on fluorescence intensity.
chromate concentration: 6.6×10^{-2} M/dm^3
thickness: ruby film (10 μm)
synthetic ruby (0.5 mm)

IV CONCLUSION

Crystalline alumina films, type eta and alpha, with metal incorporated, were prepared by the breakdown anodic oxidation of aluminum accompaned by sparking discharge. Thus, the obtained ceramic films have various color and excellent physical properties. Optical properties of these films, with chromium ions incorporated are very similar to those of the synthetic ruby prepared by Verneuil method.

REFERENCES

/1/ Tajima, S., Electrochim. Acta, 22, 955 (1977).
/2/ Lautenschlager, W., Pahlker, S.P. and Tolg, G.Z., Anal. Chem., 260, 203 (1972).
/3/ Yamada, M. and Mita, I., Chem. Lett. 795 (1982).
/4/ Mita, I. and Yamada, M., Kinzokuhyomengijitushi, 33, 421 (1981).
/5/ Mita, I. and Yamada, M. Chem. Lett. 123 (1981).
Proc. World Cong. on Met. Finish., 254 (1980).
/6/ Yamada, M. and Mita, I., Proc. Japan Cong. on Materials Research, 26th, 211 (1983), 27th, 131 (1983).